

Multivariate pattern recognition of petroleum-based accelerants by solid-phase microextraction gas chromatography with flame ionization detection

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Abstract

A novel method has been developed for the extraction, analysis and identification of petroleum-based fuels using solid-phase microextraction with analysis by GC–FID. Multivariate data analysis is employed to simplify these data allowing for more accurate classification. Principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA) are explored for their effectiveness in establishing accelerant groupings based on the current and previous ASTM International guidelines. The SIMCA models developed for the previous and current ASTM system were 98.5% and 97.2% accurate in unknown sample class prediction. SPME in conjunction with multivariate data analysis is a new approach in accelerant sampling and classification.

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1. Introduction

In 2005, 31,500 arson suspected fires caused \$664 million dollars in damage to private and public property in the United States. In addition to property, 315 lives were lost and over 2000 people were injured [1]. Although the number of fires intentionally set has been declining over the past decade [2], determining the cause still proves to be a major hurdle in solving an arson suspected fire [3].

Accelerants are used by many arsonists to increase the rate and intensity of the fire. According to arson investigators in the United States ignitable liquids are believed to be used in over 50% of all intentionally set fires [4]. In many cases petroleum-based flammable liquids are a main choice for arsonists because of the low cost and availability. Most accelerants are straight petroleum distillates including gasoline, diesel fuel, kerosene and fuel oil; modified petroleum distillates which include charcoal lighter fluid, mineral spirits, lacquer thinners, and naphtha

solvents; or a mixture of various accelerants [5]. ASTM International has established guidelines for the classification of flammable and combustible liquids [6,7] which arson investigators use to identify potential accelerants found at a fire scene. Table 1 shows the previous and current classification system. The previous numeric classification system did not adequately describe the numerous products being produced by manufacturers today leading to the most recent version. The current descriptive system gives the investigator the ability to fully describe the product by class and weight.

The complex natures of petroleum-based accelerants pose a problem for the arson investigator. Many accelerants are composed of hundreds of compounds that can make identification of fire debris very difficult. Also, the restrictive rules set forth by the legal system on the admissibility of scientific testimony have given rise to frustration for the arson investigator. Three steps were determined to be of importance for admissibility of arson expertise in today's legal system. First, inferred information must be kept separate from scientific data. Inference of information by an investigator has the potential to influence the outcome of the scientific data. Next, analytical methods must show repeatability [8]. In accordance with the *Daubert* factors,

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Table 1
ASTM International flammable and combustible liquid classification systems

Class number	Class name	Example	
Previous classification system			
1	Light petroleum distillates	Naphthas, pocket lighter fuel	
2	Gasoline	Gasoline, gasohol	
3	Medium petroleum distillates	Mineral spirits, charcoal lighter fluid	
4	Kerosene	No. 1 fuel oil, Jet-A fuel	
5	Heavy petroleum distillates	No. 2 fuel oil, diesel fuel	
0	Miscellaneous		
0.1	Oxygenated solvents	Alcohols, ketones	
0.2	Isoparaffinic products	Copier toners, specialty solvents	
0.3	Normal alkanes	Solvents, candle oils	
0.4	Aromatic solvents	Xylene, insecticide solvents	
0.5	Naphthenic/paraffinic	Lamp oils, insecticide solvents	
Class name	Light (C ₄ –C ₉)	Medium (C ₈ –C ₁₃)	Heavy (C ₈ –C ₂₀)
Current classification system			
Gasoline	Fresh gasoline in the range of C ₄ –C ₁₂ , including gasohol		
Petroleum distillates	Camp fuels	Charcoal starters	No. 1 & 2 fuel oils
Isoparaffinic products	Aviation gas	Copier toners	Specialty solvents
Aromatic products	Xylene/toluene	Fuel additives	Cleaning solvents
Naphthenic/paraffinic	Solvents	Lamp oils	Insecticide solvents
Normal alkane products	Pentane	Candle oils	Copier toners
De-aromatized distillates	Fuel additives	Metal cleaners	
Oxygenated solvents	Alcohols/ketones	Industrial solvents	
Other/miscellaneous		Single component products/turpentine	

determined by the U.S. Supreme Court, a known or associated rate error, peer review and publication lead to a degree of acceptance by the scientific community [9,10]. Finally, full-scale burns and models must be used to reconstruct fires [8]. Additional information on fire origin and cause may be determined as well as providing complementary information to the analytical data obtained [9].

Various sampling techniques have been developed to handle the multitude of debris collected at a fire scene. Traditionally, vacuum and steam distillation have been the sample preparation of choice for complex matrices. However, the time involved and/or use of hazardous solvents out-weigh the benefits [11]. Solvent extraction has also been evaluated as an effective sample preparation technique. Dichloromethane [12], alkanes [13–15], ethers and carbon disulfide [15–18] have all been explored for use in solvent extraction with varying success. Likewise, direct headspace has been used for its ease of use in a UV-spectroscopy study of accelerant vapors [15], yet compounds that are not UV absorbent are unable to be studied eliminating many petroleum-based compounds. Also, collection of analytes on an absorbent material before analysis has been widely evaluated. Activated charcoal strips [16–18] and Tenax[®] [19,20] have been the most commonly used absorbents. Hazardous solvents or additional thermal desorption equipment are needed with the use of the absorbent material increasing cost and hazards.

Since the introduction of solid-phase microextraction (SPME) by Pawliszyn in the early 1990s [21] solventless sampling techniques have been gaining interest [22–27]. Arson researches have explored SPME for the extraction of volatile organics from accelerants. Furton and co-workers [26,28–30] have done extensive research on the recovery and analysis of

accelerants from fire debris using SPME. Headspace and partial headspace recovery of analytes was reported to be effective for a wide range of molecular weights when water was added to the debris [26]. When compared to activated charcoal strips, SPME was found to have equal or greater sensitivity in identifying the accelerants studied [31,32]. The lack of solvents and the ability to use the gas chromatograph's injection port for thermal desorption makes SPME the ideal sampling device.

Interferences resulting from pyrolysis of common household items have also been a concern while investigating fire debris. In some cases the debris can have similar characteristics to that of the accelerants. Most methods have been examined for matrix interferences pre and post burn. Of these matrices, synthetic carpets are most likely to produce accelerant-type hydrocarbons after pyrolysis. Polyolefin-piled carpet showed no similar components with accelerants when charred in the open air [12]. Many matrices have been found to not interfere in the characteristic accelerant response region [17,18,30,33,34]. Similarly, accelerant residue can be identified on matrix when high enough quantities of accelerant remain after the pyrolysis [19].

Interpretation of the complex data obtained from an arson suspected fire has required the experience of a trained analyst. The chromatograms obtained from the arson debris are often visually compared to standards. Much like a fingerprint, the chromatograph of each accelerant is very distinctive. Small changes in the "fingerprint" could lead to misinterpretation of the chromatogram and misidentification of the accelerant. However, multivariate data techniques are a powerful tool in interpreting complex data matrices. Hierarchical cluster analysis (HCA), principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA) are both effective

in the simplification of complex data. HCA compares the difference between sample distances to determine similarity. The closer a sample is to another the more likely it is related to that sample than one that is further away. PCA is the manipulation of complex and often interrelated data into uncorrelated variables, principal components (PCs), which represent the variation present in the original data. The first PC represents the maximum amount of variation present in the original data. Each additional PC is orthogonal to the one preceding and accounts for the maximum amount of variation remaining in the data set. SIMCA uses PCA to determine the shape and orientation of confidence envelopes for samples of each class. Sample training sets are divided into separate classes where principal components are determined for each individual set of classes. Future samples (predictions) are compared to these confidence envelopes to determine which if any class they belong [35]. The graphical representation of the data displayed with each data analysis method allows for easier interpretation and visual correlations of the data. HCA, PCA, SIMCA and other multivariate techniques have been applied to simplify complex data systems in many areas including; chromatography [12,36,37], spectroscopy [3,38], bio-chemistry [39,40], environmental chemistry [41,42], food chemistry [43,44], as well as numerous other industrial applications [45–47].

In this study, we report the effectiveness of headspace SPME as a solventless sampling technique for the recovery of accelerants. Optimal sampling conditions were determined for a variety of accelerants. Multivariate data analysis is employed for identification and classification of accelerants using the SPME data. PCA can be combined with SIMCA to effectively predict sample class and properties. Both the previous and current ASTM International accelerant classification system can successfully be modeled with the methods explored.

2. Experimental

SPME fibers (30 μm polydimethylsiloxane, PDMS-30) purchased from Supelco (Bellefonte, PA) were used for the extraction of the accelerant samples studied. A total of 130 accelerants were examined and initially assigned to five classes based on the previous ASTM Flammable and Combustible Liquid Classification System [6]. All gasoline, diesel fuel and kerosene samples were provided by the County of Summit, Ohio Fiscal Office with complete bills of lading to identify fuel supplier and fuel delivery date. The remaining accelerant samples were purchased from local hardware and auto parts stores. A complete list of accelerants used can be obtained from the authors. A 74 mL vial equipped with a septa had 300 μL of accelerant added and placed into a temperature controlled water bath. SPME conditions were determined for absorption time and temperature as well as desorption time. This was achieved by exposing the fiber to the vial headspace between 5 and 50 min for various accelerants. The water bath was adjusted between 20 and 45 $^{\circ}\text{C}$ to achieve maximum absorption. Analyte removal from the fiber occurred by thermal desorption in a 270 $^{\circ}\text{C}$ injection port of the GC. Complete desorption of the analytes were determined through exposure times varying from 10 to 90 s.

Samples were analyzed using a Hewlett-Packard (HP) 5890 gas chromatograph (GC) with a flame ionization detector (FID) (Agilent, Palo Alto, CA) with data collection handled using GC Workmate (Willstein Scientific, Wilmette, IL). A 50 m \times 0.2 mm \times 0.5 μm PETROCOL DH 50.2 capillary column (Supelco) was used. A multi-step temperature program accomplished the desired separation. The initial temperature of the GC oven was 30 $^{\circ}\text{C}$ and held for 1 min. The temperature was increased from 30 to 220 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C min}^{-1}$ and held at 220 $^{\circ}\text{C}$ for 5 min. The temperature was then increased from 220 to 300 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$ and held for a final 5 min. The total run time was 57 min. A 0.75 mm injection sleeve was used for all SPME injections. The flow of the carrier gas was 1.0 mL min^{-1} nitrogen (Praxair Inc., Danbury, CT) and purged at 1 min.

After initial GC analysis, preprocessing of the data was needed prior to performing the multivariate analysis. An in-house program was written to calculate a response versus time profile of the raw GC data. Summation intervals of 30 and 60 s were examined for the HCA and PCA studies. The range of 180–3420 s was divided into 57 and 114 equal parts and the signal intensity was summed to represent a new variable in the final data matrix. All data was normalized using ASTM D2887 quantitative calibration mix (Supelco) as an external standard. Run to run retention time errors were corrected with comparison to the retention times of the standard. Peak area percentages were used as a means to eliminate absorption differences between samples. Response was normalized as a percentage of the total to eliminate variations due to fiber differences. SIMCA-P 11 (Umetrics Inc., Kinnelon, NJ) was used to perform all PCA and SIMCA calculations on the auto-scaled data. Leave-one-out validation was used to test the ability of the SIMCA models to classify accelerants according to the ASTM classification systems.

3. Results

SPME extraction equilibrium was determined by exposing the PDMS-30 fiber to the accelerants for known times between 5 and 50 min. Analyte absorption reached a maximum after 30 min of exposure to the headspace (Fig. 1a). Multiple extraction temperatures were also analyzed for the rapid absorption of the compounds of interest. Maximum absorbance (Fig. 1b) was achieved at 30 $^{\circ}\text{C}$ for the accelerants studied. Likewise, maximum desorption of the analytes from the fiber was determined. The fiber was exposed to the 270 $^{\circ}\text{C}$ injection port with times varying from 10 to 90 s to determine when complete removal of the analytes occurred (Fig. 1c). Desorption reached a maximum after 60 s of exposure to the heated injection port.

Baseline variations were removed in the preprocessing steps before multivariate analysis through normalizing all chromatograms to a starting baseline intensity of zero. Influence of the baseline signal could then be kept to a minimum in any further analysis. Large amounts of collected information (~ 8000 points per chromatogram) require the reduction of data into a more manageable size (114 and 57 variables) through summation of the signal intensities. Summation intervals of 30 and 60 s were examined to determine the most effective

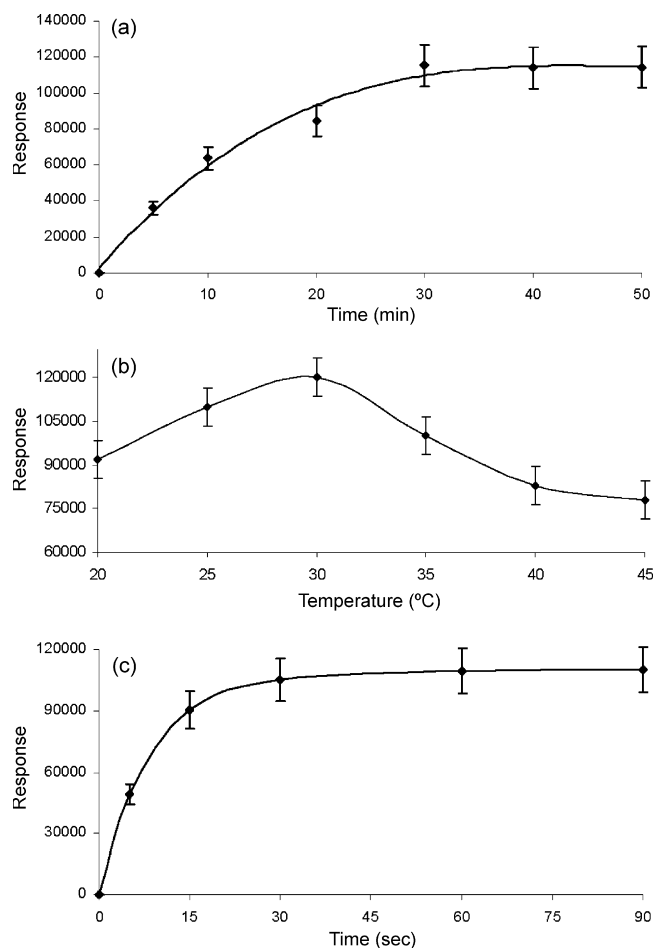


Fig. 1. PDMS-30 extraction equilibrium time profile (a). PDMS-30 extraction equilibrium temperature profile (b). PDMS-30 desorption time at 270 °C (c).

data preprocessing. Multivariate analysis has been shown to be effective on complex systems with the use of signal summations allowing for faster calculations [12]. Fig. 2 shows chromatograms of the five representative accelerant classes. The loadings plot (Fig. 3) displays the correlation between variables as well as variable influence on particular sample groups when compared to the PCA scores plot. Of the original 114 variables 28 were found to have no significant effect and were removed, reducing the size of the data set. A response was not observed in the first 3 min as well as the last 3 min of the chromatogram corresponding to 12 variables allowing these to be eliminated further reducing the number of variables examined. The remaining 16 variables did not add useful information to the classification. Overlapping variables on the loadings plot indicates redundant information is contained in the variables in question. Elimination of all but one of the variables reduces any bias resulting from repeated information.

Comparison of the ASTM D2887 calibration mixture to the PCA plots allowed correlations between accelerant groupings and weight to be determined. The calibration standard contains a hydrocarbon mixture from C₄ to C₂₈. Retention times for light, medium, and heavy accelerants were established using this mixture. Compounds up to C₈ (light) eluted from the column prior to 20 min, C₈–C₁₂ (medium) had retention of less than 32 min,

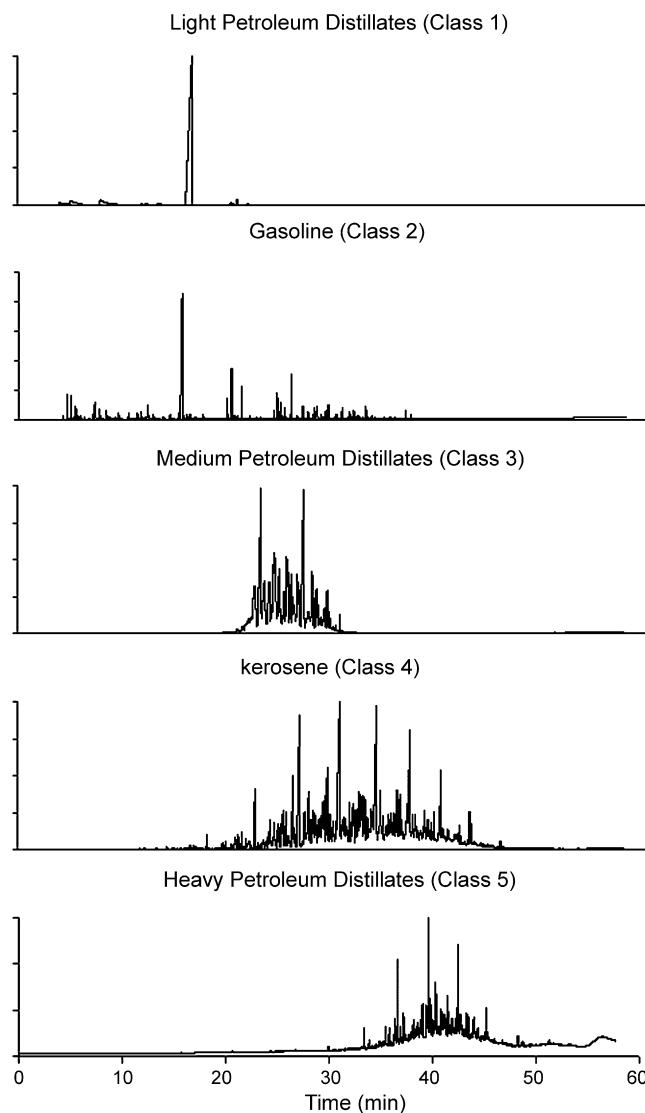
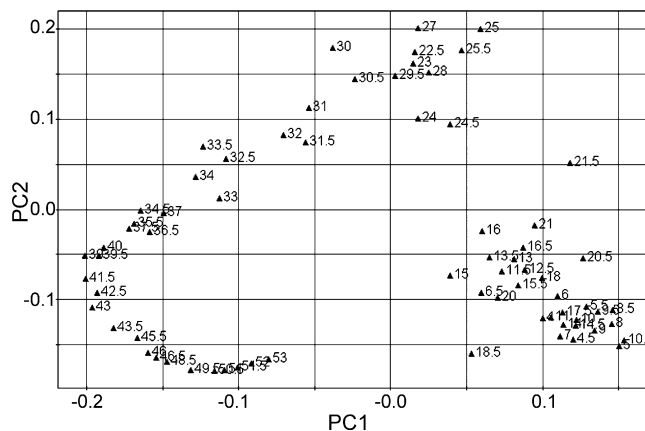


Fig. 2. Representative GC chromatograms of the five previous ASTM accelerant classes.

and heavy petroleum distillates (C₁₂–C₂₈) eluted after 32 min. The groupings in the scores plot correlate to variables in the loading plot. Class 1 accelerants cluster in the same region as variables 6–15 min. This would place them in a light petroleum



distillate range. Similarly Class 3 (MPD) cluster in a region influenced by variables 22–30 min. Gasoline (Class 2), which shares compounds with Class 1 accelerants, has chemical species eluting from 3 to 21 min. The relative small number of compounds present in Class 1 accelerants and their high volatility result in clustering independent of gasoline while still sharing similar volumes.

The data was examined using HCA to determine any initial patterns that could be observed between the various samples studied. Complete linkage of the accelerant data (Fig. 4) is more effective in the grouping of accelerants according to the previous ASTM classification system; however overlap of class characteristics still exists with this model for both summation intervals. Gasoline (Class 2) clustered mainly in one group toward the bottom of the dendrogram and had only a slight amount of similarity with some Class 4/5 accelerants. Heavy petroleum distillates and kerosene (Classes 4, 5) commingled in the dendrogram as expected because they share many characteristic compounds. ASTM International has grouped these classes together in the current classification system eliminating any concern of dendrogram overlap. Complete linkage takes advantage of the furthest distances between the groups preventing less cross-class similarities unlike single link which relies on points of closest spatial distance.

PCA was performed with the auto-scaled data to examine the potential groupings of the five classes of accelerants assigned by ASTM International. Both summation intervals were exam-

ined by PCA to determine the most effective preprocessing method. Grouping of accelerants occurred for both summation intervals with slight improvement when the 30 s data matrix was used. The resulting 30 s summation scores plot (Fig. 5a) of the five classes of accelerants is shown. The first six PCs accounted for 71.7% of the variance contained in the original data. Accelerant groupings are also observed with analysis by PCA (Fig. 5b) for the current ASTM International classification system. Six main groups were observed in the samples analyzed. Petroleum distillates were classified into subgroups (light, medium, heavy) as specified by ASTM. Other/single component products were also observed to cluster in their own class. Not every class of accelerant was represented in the

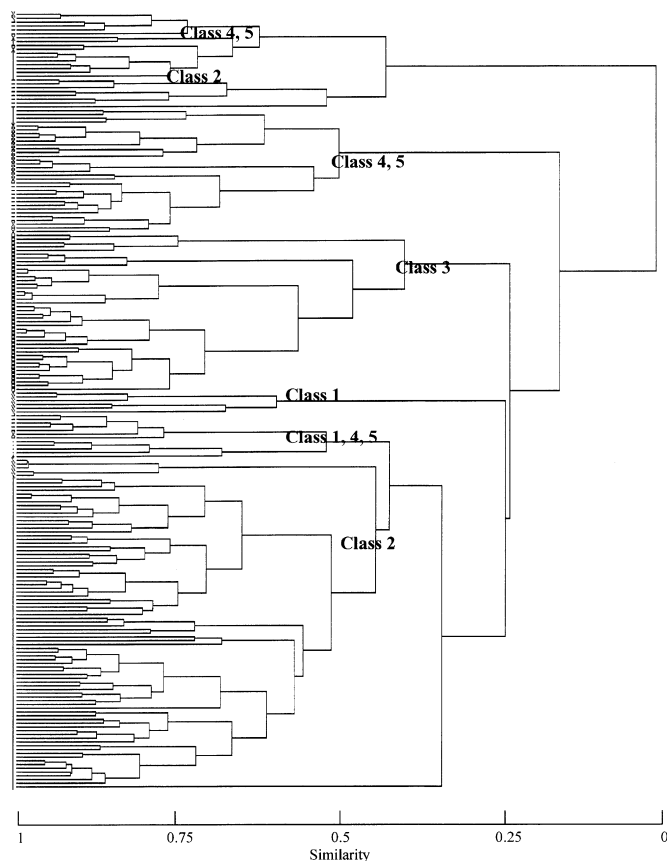
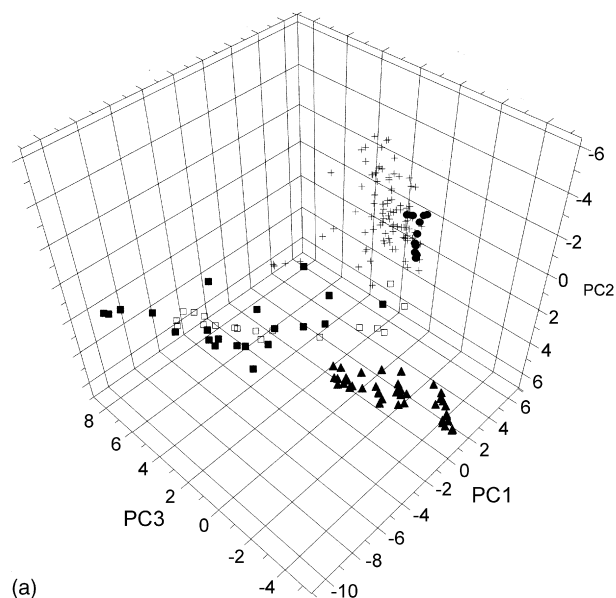
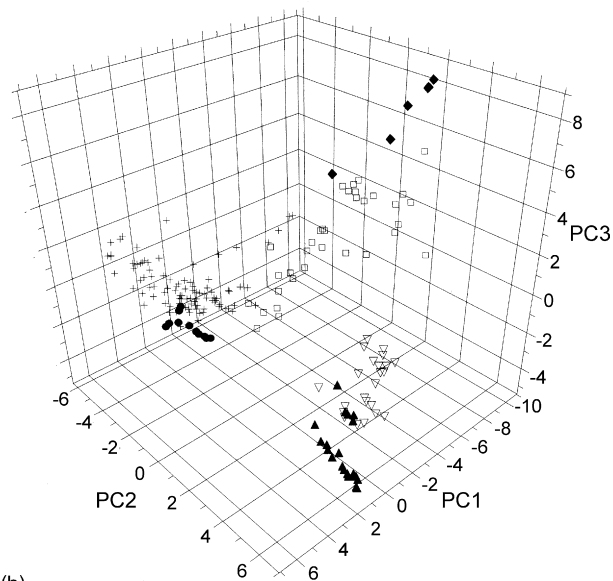


Fig. 4. HCA dendrogram plot of autoscaled accelerant data.



(a)



(b)

Fig. 5. Accelerant PCA plot based on previous ASTM classification system (●) Class 1; (+) Class 2; (▲) Class 3; (□) Class 4; (■) Class 5 (a). Accelerant PCA plot based on current ASTM system (+) Gasoline; (▽) LPD; (▲) MPD; (□) HPD; (◆) Medium aromatic; (●) Other/single component (b).

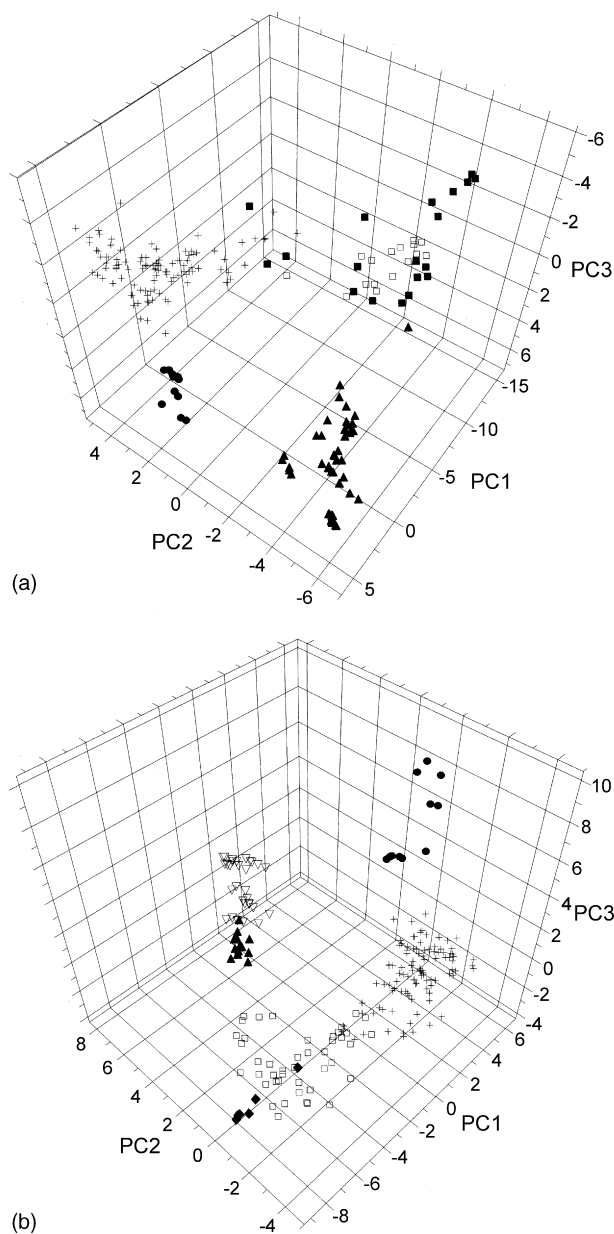


Fig. 6. Accelerant SIMCA model based on the previous ASTM classification system (●) Class 1; (+) Class 2; (▲) Class 3; (□) Class 4; (■) Class 5 (a). Accelerant PCA plot based on current ASTM system (+) Gasoline; (▽) LPD; (▲) MPD; (□) HPD; (◆) Medium aromatic; (●) Other/single component (b). PCA confidence envelopes determined for each individual class to calculate SIMCA models.

data, however strong correlations are contained in the classes examined.

A PCA for each individual class in the data set was performed and a sufficient number of PCs was retained to account for the most amount of variation in each individual class. The SIMCA model for both the previous and current ASTM systems were then calculated based on the PCA analysis determined for the individual classes. Four clusters are visible out of the five ASTM accelerant groups modeled (Fig. 6a) in which Classes 4 and 5 overlap volumes in the SIMCA model. The current ASTM classification system was also modeled with a SIMCA plot (Fig. 6b). Heavy petroleum distillates, Class 4 and 5 of the previous sys-

tem, have a strong correlation in the SIMCA plot clustering in a tight volume. Rotation along axis provide for each cluster to distinguish itself from the others. Overlap between light and medium petroleum distillates occurs for products sharing chemical characteristics. Leave-one-out validation was used to test the reliability of the SIMCA models. The reliability of the model predictions is displayed in Table 2. Leave-one-out validation correctly classified all training data for both systems. One sample belonging to Class 4 was incorrectly classified and one sample belonging to gasoline and medium aromatic were misclassified in the test data.

4. Discussion

Headspace SPME is an effective tool for extracting the volatile and semi-volatile components of accelerants and has been found to be more effective than direct sampling of similar compounds [26]. Direct absorption of analytes from some solutions has the potential to damage the fiber coating causing swelling and dissolving the epoxy glue holding the fiber [48]. An extraction time of 30 min was found to be effective in the absorption of the compounds of interest. Longer extraction periods result in absorptive extraction of the analytes and therefore reproducible results. Shorter extraction times result in a higher concentration of analyte at the headspace/fiber partition interface and adsorptive extraction which is less reproducible. An increase in extraction temperature results in a higher concentration of compounds in the headspace. The optimal extraction temperature of 30 °C was used for all analysis. An increase in temperature results in a higher concentration of analytes in the headspace. However, the same increase in temperature shifts the equilibrium of the compounds from the fiber to the headspace reducing the amount extracted. A balance between the maximum concentration of analytes in the headspace and maximum absorption onto the fiber should be achieved for reproducibility and sensitivity. This balance results in the extraction and concentration of compounds being merged into a single step. Complete desorption of the analytes from the fiber occurred after 60 s of exposure to the injection port. The introduction of analytes into the GC as well as the cleaning of the fiber is also combined into one step allowing for faster analysis. Further exposure to the heated injection port could potentially shorten the fiber's effective lifetime.

Approximately 8000 data points were collected for each sample and reduced to 114 summation intervals making the data set more manageable. Thirty second summation intervals were found to greatly decrease the computer calculation times and at the same time left enough information for proper classification. Previously, large data sets forced researchers to choose between data and time due to lack of computing power [12], but advances in computers allow larger data sets to be examined without the loss of valuable time. Many variables were eliminated from the data set after visual inspection. No response was observed for the first 3 min of any accelerant as well as the last 3 min of the GC temperature program. The final 3 min of the temperature program ensured all analytes had been removed from the column prior to subsequent analysis.

Table 2
SIMCA models and predictions

Class	No. of training samples	No. of PCs	Variance captured (%)	Correct classification
Previous ASTM classification system				
Class 1	14	3	93.2	7/7
Class 2	66	10	86.0	33/33
Class 3	22	9	93.6	11/11
Class 4	12	3	83.7	6/6
Class 5	16	3	80.6	7/8
Class	No. of training samples	No. of PCs	Variance captured (%)	Correct classification
Current ASTM classification system				
Gasoline	66	3	80.7	32/33
LPD	6	3	82.2	3/3
MPD	16	6	93.0	8/8
HPD	34	5	88.2	17/17
Aromatic	8	2	89.9	3/4
Other	14	3	93.1	7/7

The previous ASTM classification system is modeled by PCA. Clusters are observed which correspond to the five classes studied. Class 1 and 2 and 4 and 5 tend to cluster together as observed in Fig. 5a. These cross-class characteristics are due to the similarity of compounds between the classes. The first two classes overlap volumes in the PCA model because they share similar compounds in the C₈–C₉ region of the chromatograms. The shared region contained the major peak in both classes of accelerants resulting in a large correlation when examined by PCA. Class 4 and 5 also share similar compounds throughout the entire mass range. The elimination of separate classes in the current system resolves any classification problems for these accelerants. Likewise, cross-class naming is permitted in the new classification system when accelerants possess characteristics of multiple weight ranges. A light-medium petroleum distillate is observed containing compounds C₇ through C₉ which overlaps both weight ranges.

These data have shown that the use of SIMCA for the prediction of accelerant class has the potential to be an effective method. Diesel and kerosene overlap confidence envelopes showing many similar characteristics exist between the two groups. These characteristics are confirmed in the new classification system and are modeled in Fig. 6b. The same cross-class characteristics are observed for light-medium petroleum distillates as they were in the PCA model. The SIMCA model developed, based on the previous system, successfully classified 98.5% of the samples examined. The sample misclassified belonged to Class 5 and did not show any correlation to the other classes leading to the conclusion that it is an outlier. The SIMCA model based on the current system was able to correctly classify 97.2% of the samples examined in the test set. Like with the previous system, the samples did not show any correlation to other classes making them outliers in the data set.

5. Conclusions

SPME is an effective tool for the sampling of accelerants used to commit arson. Optimization on SPME conditions leads to reproducible results and high levels of sensitivity. Pattern

recognition techniques can be used to successfully classify the accelerants according to both the previous and current ASTM International guidelines. Problems are observed in the previous ASTM system in classifying Class 4 and 5 accelerants due to their similar chemical properties. This issue is resolved with the most recent ASTM system placing the two groups together. SIMCA can be used as a predictor of accelerant class for the products studied and as the number of accelerants examined increases the effectiveness of the models will continue to increase. The current ASTM classification system allows the arson investigator to better describe the accelerants detected.

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